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14. ABSTRACT

Metal oxide and supported-Pt catalysts were developed for complete oxidation of volatile organic compounds (VOCs) and other solvent-derived organic vapors (OVs) in air at relatively low temperatures. The goal for this work is to produce a simple, cost-effective technology for reducing the concentration of organic contaminants in air to acceptable levels before the air is released into the atmosphere or recirculated. Specific applications include ventilated work spaces for spray painting and engine maintenance, indoor air decontamination, dry cleaning, food processing, fume hoods, residential use, and solvent-intensive industrial processes. Catalyst powders and monolith-supported catalysts were screened for conversion of 1-butanol, toluene, and methyl ethyl ketone to carbon dioxide and water. ... However, the catalysts quickly deactivated in the presence of sulfur and phosphorus.

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Catalytic Oxidation of Volatile Organic Liquids

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Abstract: Metal oxide and supported-Pt catalysts were developed for complete oxidation of volatile organic compounds (VOCs) and other solvent-derived organic vapors (OVs) in air at relatively low temperatures. The goal for this work is to produce a simple, cost-effective technology for reducing the concentration of organic contaminants in air to acceptable levels before the air is released into the atmosphere or recirculated. Specific applications include ventilated work spaces for spray painting and engine maintenance, indoor air decontamination, dry cleaning, food processing, fume hoods, residential use, and solvent-intensive industrial processes. Catalyst powders and monolith-supported catalysts were screened for conversion of 1-butanol, toluene, and methyl ethyl ketone to carbon dioxide and water. The concentration of OVs in the feedstream was maintained at approximately 100 ppmv, and the space velocity was between 6,000 and 18,000 h^{-1}. Metal oxide catalysts without Pt generated complete conversion of 1-butanol to CO_2 at 150°C, 69% conversion at 100°C, and 15% conversion at 80°C. For toluene, complete conversion was achieved at 200°C, and greater than 75% conversion at 150°C. Addition of Pt to the metal oxide compositions typically lowered the temperature for a given OV oxidation rate by at least 20–50°C. Catalysts deposited onto standard commercial cordierite monoliths retained their composition and activity, and were stable in humid air, as well as nitrogen- and chlorine-containing OVs. However, the catalysts quickly deactivated in the presence of sulfur and phosphorus.

CE Database subject headings: Abatement and removal; Oxidation; Volatile organic chemicals; Vapor; Temperature effects.

Introduction

Increasing concern over detrimental environmental and health effects resulting from emission of volatile organic compounds (VOCs) has led to stricter emission regulation standards, and has fueled efforts to identify efficient and economical methods for VOC abatement (USGPO 2002). Conventional noncatalytic methods for removing VOCs from gaseous waste streams include incineration (Anguil 1998) and carbon adsorption (Parmele and Kovalcson 1998). While both of these methods are effective, they require either special equipment and high temperatures, or secondary processing steps that are expensive to implement and maintain. Conversely, catalytic destruction of VOCs potentially offers a less complicated and more economical and efficient emission control system than incineration or adsorption. Catalytic destruction occurs at much lower temperatures than incineration, and the reactors are simpler and cheaper to construct and operate.

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Furthermore, unlike adsorption methods, catalytic destruction is a one-step process for complete combustion of VOCs.

Traditionally, catalysts employed for destruction of VOCs and other organic vapors (OVs) are either metal oxides or noble metals supported on relatively inactive materials such as Al_2O_3 or SiO_2 (Spivey 1987). While noble metal catalysts have higher activity for OV destruction, metal oxides are cheaper and generally have greater resistance to poisoning from feedstream components. As with noble metal catalysts, metal oxides are active for combustion of OVs with a range of organic functional groups (Miller and Wilhoyte 1967; Wasfi et al. 1978; Gonzalez and Nagai 1985; McCabe and Mitchell 1986; Spivey 1987; Gangwal et al. 1988; Barresi and Baldi 1994). For example, the oxides of Fe, Mn, Mg, Ni, Co, V, Zn, Ti, Mo, Cr, and Cu were used for the combustion of alcohols, aldehydes, alkanes, olefins, methane, and carbon monoxide at temperatures between 250 and 450°C (Spivey 1987). Dispersion of noble metals such as Pt or Pd onto metal oxides can reduce the catalytic combustion temperature to a range between 100 and 200°C, depending on the specific catalyst system and OV. However, even with noble metal catalysts, the temperatures required to attain high activity generally are well above 100°C. A significant reduction in operating cost can be realized by lowering the temperature range for activity of metal oxide catalysts or by achieving catalytic combustion at near-ambient temperatures with noble metal catalysts.

The catalytic properties of CeO_2-based materials were thoroughly studied, and improvements in metal oxide oxidation catalysts resulted from strategically modifying CeO_2 with other metal oxides (Liu and Flytzani-Stephanopoulos 1995a, b; de Leitenburg et al. 1996; Trovarelli 1996; Terribile et al. 1999; Trovarelli et al. 1999). Unmodified CeO_2 is active for oxidation of CO with light-off temperatures (50% conversion) above 300°C (Liu and Flytzani-Stephanopoulos 1995a). However, by adding La to promote oxygen vacancies, and a small quantity of Cu (1 at. %), as either bulk CuO or incorporated into the structure, the light-off

temperatures for CO oxidation were reduced below 100°C (Liu and Flytzani-Stephanopoulos 1995a). Strong interactions between transition metal dopants and metal oxides are largely responsible for the enhancement in catalytic activity. It is perceivable that active sites are formed by highly dispersed clusters of transition metal atoms and ions that promote oxidation at the phase boundary between the cluster and metal oxide (Liu and Flytzani-Stephanopoulos 1995a).

Noble metal oxidation catalysts also were studied for low-temperature oxidation of CO (Stark and Harris 1983; Haruta et al. 1989; Haruta et al. 1993; Hoflund et al. 1995). In the early 1980s, Stark et al. demonstrated that Pt/SnO_x was very active for CO oxidation (Stark and Harris 1983), and Hoflund et al. compared this catalyst to Au/MnO_x (Hoflund et al. 1995). The authors found that Au/MnO_x was more active than Pt/SnO_x and produced nearly 60% conversion of CO to CO_2 at only 35°C (Hoflund et al. 1995). Further advancements were achieved by Haruta et al. who demonstrated activity for the oxidation of CO below 0°C using highly dispersed Au on oxides of Fe, Co, and Ni (Haruta et al. 1987; Haruta et al. 1993; Hoflund et al. 1995). Since Au alone is relatively inactive toward oxidation, and the metal oxides are active for CO oxidation only at elevated temperatures, the results obtained by Hofland et al. and Haruta et al. underscore the synergistic relationship between the noble metal and metal oxide support. It is anticipated that optimizing this synergy will be critical for achieving near-ambient activity for VOC oxidation.

The objective of this work was to develop metal oxide and noble metal catalysts to reduce catalytic combustion temperatures of OVs. The performance of several proprietary catalysts with and without Pt for complete destruction of representative OVs are presented and compared to analogs supported on commercial ceramic monoliths. Additionally, catalyst stability in the presence of potential feedstream poisons is demonstrated.

Experiment

Catalyst Compositions

Catalysts in this study are represented as $nPt/(M'O_y)_x(CeO_2)_{1-x}$, where n = weight percent (wt%) between 0 and 5, M' is one or more transition metals from the group Mn, Fe, Co, Cu, Zr, and $0 < x < 1$. The catalysts either were in the form of metal oxide mixtures or transition metal doped CeO_2. The catalyst compositions expressed in terms of metal atomic fraction were designated as follows:

- $Ce_{0.475}Zr_{0.050}Mn_{0.475}O_y$ (EL-1),
- $Ce_{0.45}Zr_{0.05}Mn_{0.45}Cu_{0.05}O_y$ (EL-2),
- $Ce_{0.80}Zr_{0.05}Cu_{0.15}O_y$ (EL-3),
- $Ce_{0.475}Zr_{0.050}Cu_{0.475}O_y$ (EL-4),
- $Ce_{0.10}Mn_{0.45}Co_{0.45}O_y$ (EL-5),
- $Ce_{0.5}Fe_{0.1}Cu_{0.4}O_y$ (EL-6),
- $Ce_{0.8}Mn_{0.2}O_y$ (EL-7),
- $Ce_{0.95}Zr_{0.05}O_y$ (EL-8),
- $Ce_{0.50}Co_{0.25}Cu_{0.25}O_y$ (EL-9),
- $Ce_{0.30}Zr_{0.05}Mn_{0.65}O_y$ (EL-10),
- $Ce_{0.10}Mn_{0.45}Cu_{0.45}O_y$ (EL-11), and
- $Ce_{0.3}Mn_{0.7}O_y$ (EL-12).

Additional details regarding these materials are found in S. E. Roark and J. H. White [U.S. Patent No. 6,458,741 (2002)].
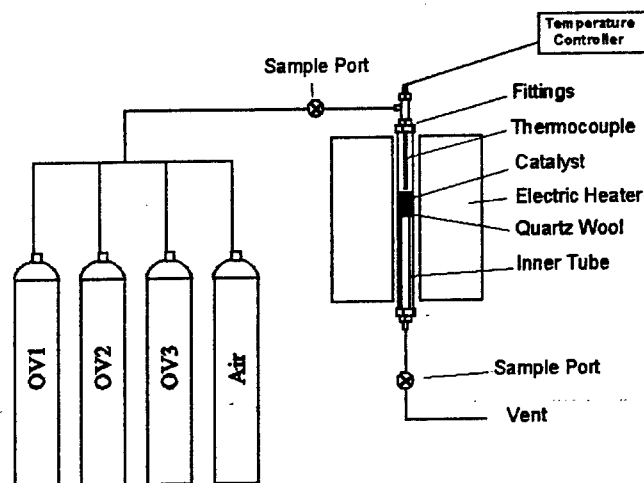

Fig. 1. Schematic diagram of the apparatus used for catalyst evaluation.

Catalyst Preparation

Powder catalysts were prepared by coprecipitation from mixtures of metal nitrates using $1M$ NH_4OH. The precipitates were filtered and washed several times with deionized water, then dried overnight at 120°C in air. The dried powders were ground, passed through a 150 μm sieve, then calcined in air at temperatures between 400 and 500°C for several hours.

Pt analogs were prepared by forming a slurry of approximately 3 g of metal oxide catalyst powder and 9 mL of a 10 mg/mL Pt precursor solution $[Pt(NH_3)_4(NO_3)_2$, Aldrich]. The slurry was mixed for 1 h, then roto-evaporated under vacuum at 70°C. The resulting powder was dried at 120°C in air, then reduced at 350°C under 10 vol % H_2 (bal. Ar).

Supported catalysts were prepared on commercial cordierite monoliths (Corning) with 400 cells/in^2. Test monoliths had a diameter of 14 mm and height of 25 mm. Monolith samples were washed several times in methanol and dried at 200°C for 5 min prior to coating with the catalyst. A layer of Al_2O_3 was applied to the bare monoliths to increase surface area. This step was accomplished by repeatedly dipping the monolith into a boehmite solution followed by drying at 120°C for 2 h. After three applications, the coated monolith was calcined for 2 h at 400°C. This procedure increased the surface area from 2.4 ± 0.3 m^2/g for the bare monolith to greater than 20 m^2/g with the Al_2O_3 coating. Catalysts were applied to the Al_2O_3-coated monoliths by repeated dipping in an aqueous nitrate precursor solution followed by drying and calcining in air at 400–500°C for 5 h to produce the corresponding oxides.

Catalyst Evaluation

Fig. 1 shows a simplified schematic diagram of the plug-flow apparatus used for catalyst evaluation. The apparatus incorporated four reactors, each consisting of a furnace surrounding a 4 mm i.d. (powder samples) or 14 mm i.d. (monolith samples) quartz tube containing the catalyst sample. Catalyst samples were held in place by pads of quartz wool and a section of a narrow inner tube. OVs were introduced into the system from cylinders of 200 parts per million by volume (ppmv) OV/air mixtures (AirGas). The concentrations typically were adjusted to 100 ppmv by mixing the OV supply with an air supply line. Flow rates and mixing ratios were controlled by needle valves and monitored using both ball-

type and bubble flow meters. Reactor temperatures were measured and adjusted using controllers paired with thermocouples inserted in the quartz reactor tubes to a height touching the top of the catalyst bed.

The space velocity (SV) was calculated according to

$$SV = \frac{F_T}{V_c} = \frac{F_T}{(d/2)^2 \pi h} \qquad (1)$$

where F_T = total gas volume flow rate, V_c = catalyst geometric volume, d = inner diameter of the quartz sample tube, and h = height of the catalyst bed in the sample tube. Approximately 0.2 g of catalyst was used for each evaluation, which resulted in a roughly 1 cm deep catalyst bed. Based on the catalyst geometric volume, gas flow rates were adjusted to between 3 and 70 mL/min to achieve space velocities between 6,000 and 18,000 h^{-1}. For monolith-supported catalysts, the data were more conveniently expressed as a ratio of the catalyst weight to flow rate (W/F) in units of g s/cm^3. Thus for 0.2 g of catalyst on a monolith, and a flow rate of 12 mL/min, the W/F = 1.0 g s/cm^3.

Representative OVs used in this work were toluene, 1-butanol, and methyl ethyl ketone (MEK). These OVs were chosen based on their use in spray paints and general popularity as solvents. Additionally, they represent different organic functional groups, i.e., aromatic, alcohol, and ketone. Measurements of the inlet OV concentration and outlet OV and CO$_2$ concentrations were accomplished by sampling through ports located on opposite sides of the reactors. Prior to screening, catalyst samples were heated in line at 200°C overnight under flowing air. Inlet and outlet OV concentrations were determined from chromatographic peak areas using a Shimadzu GC-14A with flame-ionization detection and a 1% AT 1000 Graphpac 60/80 column (Alltech). Product CO$_2$ concentrations were determined using a Hewlett-Packard 5890 GC with thermal-conductivity detection and a CTR-1 column (Alltech).

Percent conversion values (%C) were based entirely on CO$_2$ production and calculated according to

$$\%C = \left(\frac{[CO_2]_{out}}{S[OV]_{in}}\right) 100 \qquad (2)$$

where $[CO_2]_{out}$ = outlet CO$_2$ concentration (ppmv), S = stoichiometric factor (4 for 1-butanol and MEK, and 7 for toluene), and $[OV]_{in}$ = OV inlet concentration. At low conversion values, partial oxidation products occasionally were observed; however, no attempt was made to identify these compounds. Reaction rates also were calculated from outlet CO$_2$ according to

$$Rate = \frac{F_m X_{CO_2}}{S W_{cat}} \qquad (3)$$

where F_m = total molar gas flow rate, X_{CO_2} = outlet mole fraction of CO$_2$, and W_{cat} = catalyst sample weight. Using this equation, the reaction rate was expressed in units of moles of VOC destroyed per second per gram of catalyst (mol s^{-1} g^{-1}).

Catalyst surface area was determined by the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2000.

## Results and Discussion

Metal Oxide Catalysts

Fig. 2 contains a summary of catalytic activity for conversion of 1-butanol to CO$_2$ for five powder CeO$_2$-derived catalysts, EL-1 through EL-5. For comparison, results for unmodified CeO$_2$ and a
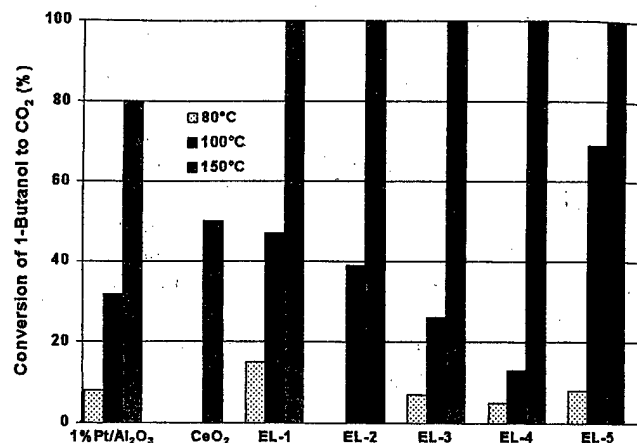
Fig. 2. Percent conversion of 1-butanol to CO$_2$ as a function of temperature for several powder catalyst compositions. The 1-butanol concentration was approximately 100 ppmv in air and the space velocity was approximately 6,000 h^{-1}. Catalyst compositions are provided in the "Experiment" section.

commercial 1%Pt/Al$_2$O$_3$ catalyst (Alfa Aesar) were included as well. The conversion values shown in Fig. 2 are averages of steady-state measurements taken after approximately 10–24 h at each temperature. Typically, the relative error in the measurements was less than 15%. The presence of Mn in the catalyst composition generally improved catalyst performance. At 150°C, the EL catalysts all achieved 100% conversion compared to only 50% conversion for unmodified CeO$_2$. The most active catalyst at 100°C was EL-5, which achieved 69% conversion. Moreover, all of the EL catalysts without noble metals performed better than commercial 1%Pt/Al$_2$O$_3$ at 150°C, and EL-1 and EL-2 performed better at 100°C as well.

Fig. 3 summarizes catalyst performance for conversion of toluene to CO$_2$. Toluene was more difficult to completely oxidize than 1-butanol and testing was performed at higher temperatures. In Fig. 3, unmodified CeO$_2$ and EL-5 again are shown, as well as four alternative compositions EL-6 through EL-9. All of the EL catalysts in the figure achieved 100% destruction of toluene at
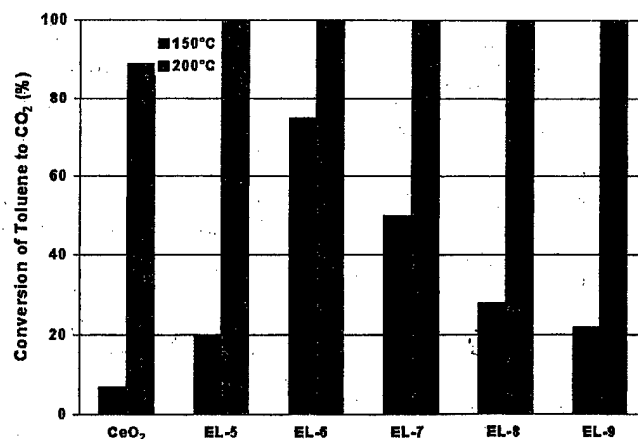
Fig. 3. Percent conversion of toluene to CO$_2$ as a function of temperature for several powder catalyst compositions. The toluene concentration was approximately 100 ppmv in air and the space velocity was approximately 6,000 h^{-1}. Catalyst compositions are provided in the "Experiment" section.

Table 1. Catalyst Surface Areas and Rates for OV Conversion to CO_2

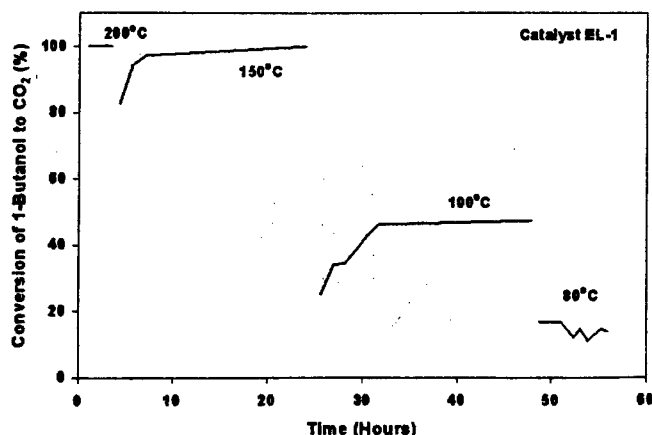| Catalyst	Surface area $(m^2/g)^a$	OV^b	Temperature (°C)	Rate $(mol\ s^{-1}\ g^{-1})$	Rate $(mol\ s^{-1}\ m^{-2})$
EL-1	89.3±0.3	1-butanol	100	1.73×10^{-9}	1.93×10^{-11}
EL-2	75.5±0.5	1-butanol	100	1.43×10^{-9}	1.90×10^{-11}
EL-3	64.1±0.4	1-butanol	100	0.956×10^{-9}	1.49×10^{-11}
EL-4	113.8±0.3	1-butanol	100	0.478×10^{-9}	0.420×10^{-11}
EL-5	125±1	1-butanol	100	2.54×10^{-9}	2.03×10^{-11}
		Toluene	150	0.735×10^{-9}	0.588×10^{-11}
EL-6	170±1	Toluene	150	2.76×10^{-9}	1.62×10^{-11}
EL-7	111±1	Toluene	150	1.84×10^{-9}	1.65×10^{-11}
EL-8	114±1	Toluene	150	1.03×10^{-9}	0.903×10^{-11}
EL-9	30.0±0.3	Toluene	150	0.809×10^{-9}	2.70×10^{-11}
CeO_2	43.6±0.1	Toluene	150	0.257×10^{-9}	0.590×10^{-11}

[a]The error in the measurement represents $\pm 1\sigma$.

[b]The OV concentration was approximately 100 ppmv in air and the space velocity was approximately 6,000 h^{-1}.

200°C, and demonstrated a significant improvement in activity relative to unmodified CeO_2. Lowering the temperature to 150°C dramatically reduced conversion for EL-5, EL-8, and EL-9; however, EL-6 and EL-7 maintained 75 and 50% conversion of toluene to CO_2, respectively. Since the EL catalysts in Figs. 2 and 3 were combinations of CeO_2 and comparatively inactive transition metal oxides, these results indicated that significant improvements in catalyst activity could be achieved through relatively minor modifications in catalyst composition. Furthermore, the dramatic increase in activity achieved by compositing metal oxides underscores the beneficial synergy between these materials for low-temperature combustion.
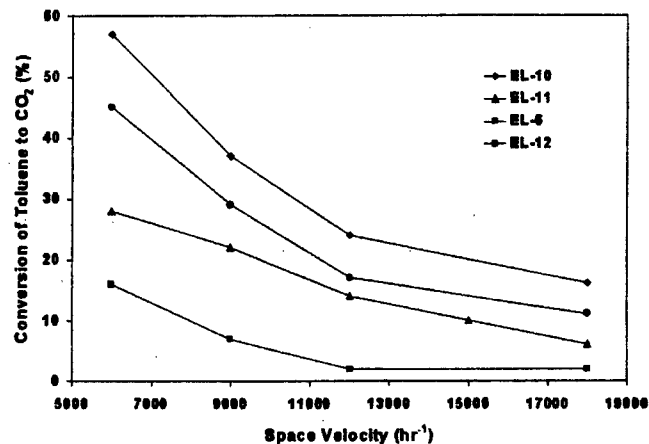
Catalyst surface areas and conversion rates are summarized in Table 1. Conversion correlated fairly well with surface area; however, the same overall trend in catalyst activity as shown in Fig. 2 still is apparent when conversion rates are normalized to the total catalyst surface area for each sample (i.e., $mol\ s^{-1}\ m^{-2}$). Furthermore, despite having high surface area, EL-4 clearly was the least active catalyst of this set. For toluene destruction, normalizing conversion rates to m^2 of catalyst surface area revealed that catalyst EL-9 was the most active composition, although the percent conversion was low.

Fig. 4 shows the general behavior of these catalysts as a function of time and temperature for OV destruction over a 56 h test period. After reducing the test temperature from 200 to 150°C, and from 150 to 100°C, there was an induction period before steady activity was established. This induction period increased with decreasing temperature, lasting about 3 h at 150°C, 6 h at 100°C, and although not apparent in this data set, as long as 24 h at 80°C for other experiments. During the induction period, only CO_2 was observed in the reactor effluent and there was a large disparity in the carbon balance between the inlet OV concentration and reactor outlet. After steady activity was established, a reasonable carbon balance was achieved and the catalyst demonstrated stable performance over the 7–20 h test period. This behavior likely was the result of temperature-dependent OV adsorption on the catalyst surface, and is characteristic of high-surface-area catalysts when the OV concentration is low (Papaefthimiou et al. 1997; Paulis et al. 2000). The increase in activity during the induction period presumably reflects surface concentration-dependent kinetics at temperatures that allow condensation. Once the surface was saturated, steady conversion was achieved and a subsequent increase in catalyst temperature resulted in an initial pulse of OV and CO_2 in the outlet that gradually diminished to a constant value. The lack of an induction period at higher temperatures (≥ 200°C) where condensation was minimized and complete or nearly complete conversion was achieved was consistent with this interpretation of these results.

Fig. 4. Conversion of 1-butanol to CO_2 as a function of time and temperature for catalyst EL-1. The 1-butanol concentration was approximately 100 ppmv in air and the space velocity was approximately 6,000 h^{-1}.

Fig. 5. The effect of space velocity on percent conversion of toluene to CO_2 at 175°C for selected catalysts. The toluene concentration was approximately 100 ppmv in air.
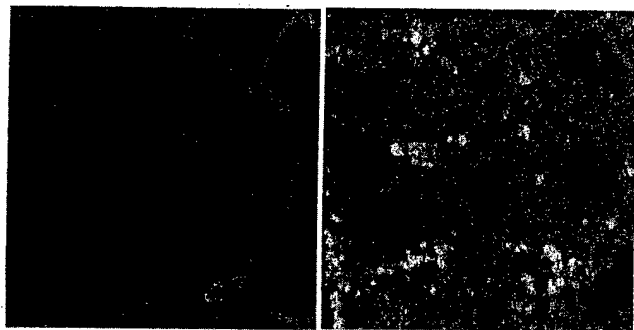
Fig. 6. Magnified images (26×) of a 13 wt% alumina coated monolith (left) and a 26 wt% EL-1 catalyst coated monolith (right).

Fig. 7. The effect of catalyst loading on surface area, percent conversion of toluene to CO_2, and rate of toluene destruction. The catalyst was EL-1. The toluene concentration was approximately 100 ppmv in air, and the $W/F \approx 1.0$ g s/cm^3. Conversion and rate measurements were obtained at 200°C.

Fig. 5 demonstrates the effect of space velocity on OV conversion for selected catalysts. For routine testing, a space velocity of 6,000 h^{-1} was chosen to enable sufficient conversion for comparing catalysts with a wide range of activity. Conversion was not highly dependent on space velocity below about 6,000 h^{-1}; however, a significant drop in conversion was observed between 6,000 and 18,000 h^{-1}. Despite this drop, the data stabilized at space velocities above approximately 18,000 h^{-1}, and substantial conversion rates still were achieved at space velocities as high as 26,000 h^{-1}.

The data presented above represent the best results obtained using catalysts without noble metals for destruction of 1-butanol and toluene, and similar results were obtained for MEK. Considering all catalyst compositions tested for destruction of these three OVs, activity for complete OV combustion generally decreased in the order of 1-butanol>MEK>toluene. A similar trend also was observed in the literature, and correlated with dissociation energies of the weakest C–H bond and surface adsorption affinity (Batiot and Hodnett 1996; O'Malley and Hodnett 1997, 1999). However, the compositions with the best performance for 1-butanol destruction were different than those with the best performance for toluene destruction. It is apparent that treating effluents containing mixtures of OVs will require either a compromise between catalyst composition and activity, or compositions will be selected based on a target contaminant in the mixture.

Supported Metal Oxide Catalysts

The catalyst compositions designated as EL-1 and EL-5 were tested deposited onto standard cordierite monoliths. Attempts to deposit slurries of catalyst powder onto support structures resulted in pore clogging and nonuniform layers with very poor catalyst adhesion. Alternatively, deposition by decomposition of nitrate precursors, as described in the "Experiment" section, gave very uniform and structurally stable films. Moreover, since this method was not subject to problems associated with selective precipitation, the target catalyst compositions were achieved easily and reproducibly. Fig. 6 shows magnified images of monolith sections before and after catalyst deposition. The section without catalyst contained 13 wt% alumina, which was barely visible at this magnification. The lack of an obvious alumina film suggested that the sol-gel deposition procedure produced an even and relatively dense coating. The image on the right shows a very thick (26 wt%) EL-1 catalyst layer with large catalyst grains and high porosity. Even at this level of catalyst loading, the coating remained adhered to the cell walls, and the cells were unobstructed through the length of the monolith section.
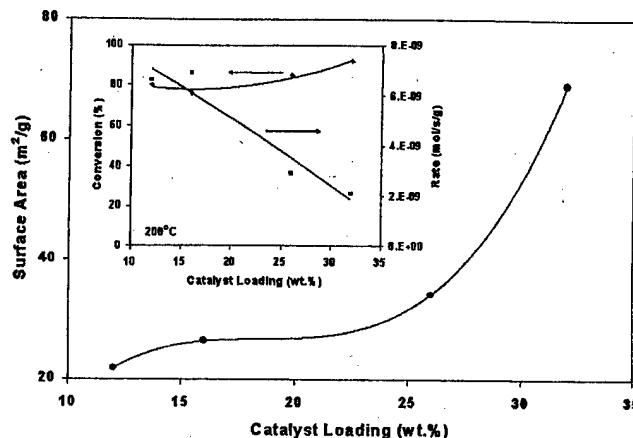
Fig. 7 summarizes the effect of catalyst EL-1 loading on surface area, percent conversion of toluene to CO_2, and the rate of toluene destruction. Rather than space velocity, W/F was used instead since the monolith-supported catalysts were different in nature from the powders. Specifically, the plug-flow reactor volume with powder samples was only 0.13 cm^3, which corresponded to a space velocity of 6,000 h^{-1} and a residence time of approximately 0.6 s at a flow of 12 mL/min. However, for monolith testing the *same* mass of catalyst was distributed over a much larger volume of 2.3 cm^3, which corresponded to a space velocity of only 300 h^{-1} and a residence time of almost 10 s. Since approximately 2 cm^3 of this total volume was empty space, space velocity calculations dramatically underestimated the activity of the catalyst materials, and W/F was deemed more representative. Fig. 7 demonstrates that as catalyst loading increased from 12 to 32%, there was a corresponding increase in surface area from 21.8 ± 0.1 to 69 ± 3 m^2/g, which approached the value for the unsupported powder of 89.3 ± 0.3. Despite these differences in loading and surface area, the percent conversion of toluene to CO_2 increased only slightly, as shown in the inset of Fig. 7. Furthermore, as also shown in the inset, the rate of toluene destruction per gram of catalyst decreased significantly as loading increased.

Monolith-supported EL-5 achieved higher percent conversion than the EL-1 analog. Both a 6 and 26 wt% EL-5 catalyst-loaded sample enabled 100% destruction of toluene at 200°C. This result was particularly significant for the 6 wt% sample since the quantity of catalyst on the monolith was only 0.055 g. The 26-wt%-loaded sample achieved 35% destruction at 150°C, which was much higher than 20% for the powder EL-5 sample shown in Fig. 3.

The reproducibility of supported catalysts enabled convenient optimization of compositions. An example is shown in Fig. 8 for destruction of toluene using a range of catalysts derived from EL-5. The composition was experimentally optimized by varying the catalyst constituents and testing activity. This range of catalysts was represented as $Ce_{0.1}Mn_xCo_{0.9-x}O_y$, and the abscissa of the plot indicates changes in the Mn and Co content with Ce held constant. The maximum in both curves occurred at $x \approx 0.45$, which corresponds to a composition of $Ce_{0.10}Mn_{0.45}Co_{0.45}O_y$. At 150°C, this sample achieved 56% conversion of toluene to CO_2,
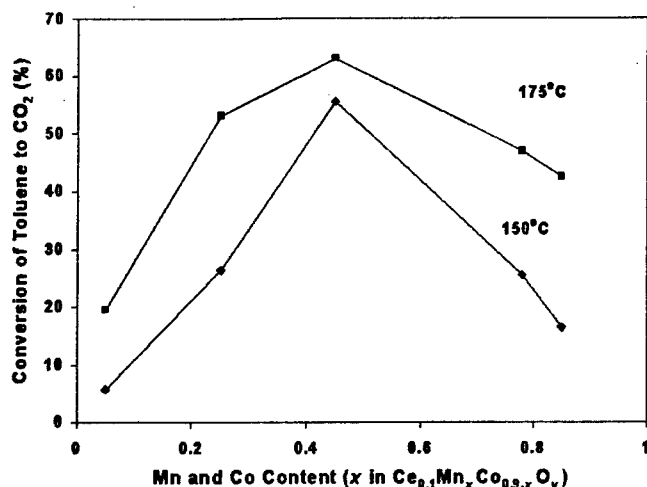
Fig. 8. Conversion of toluene to CO_2 as a function of catalyst composition for materials derived from EL-5. The toluene concentration was approximately 100 ppmv in air and $W/F \approx 1$ g s/cm^3.

compared to only 20% for an equal mass of the EL-5 powder. Similar plots independently holding Mn constant and Co constant generated equivalent results and indicated that $Ce_{0.10}Mn_{0.45}Co_{0.45}O_y$ was optimal for toluene destruction with Ce–Mn–Co–O catalysts.

Supported Platinum Catalysts

Addition of Pt to the mixed metal oxide compositions generally lowered the temperature for a given conversion rate by at least 20–50°C. Activity increased with increasing Pt content up to about 3 wt%, then stabilized between 3 and 7 wt%. Reductive pretreatment dramatically improved activity of the Pt catalysts, and as shown in Fig. 9, the conditions for reductive pretreatment greatly affected activity at low temperatures. Samples of 5 wt%Pt/ EL-1 were reduced under H_2 at 350, 500, and 700°C, then tested for conversion of 1-butanol to CO_2. Although conversion at 150°C was about the same for all three samples, as the reduction
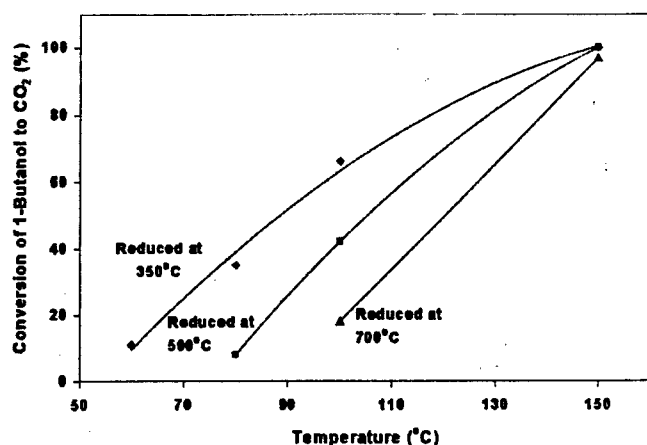
Fig. 9. The effect of reduction temperature on activity of supported Pt catalysts. The catalyst contained 5 wt% Pt supported on catalyst EL-1. The 1-butanol concentration was approximately 100 ppmv in air and the space velocity was approximately 6,000 h^{-1}. Catalysts were reduced at the indicated temperature under flowing 10% H_2/90% Ar.
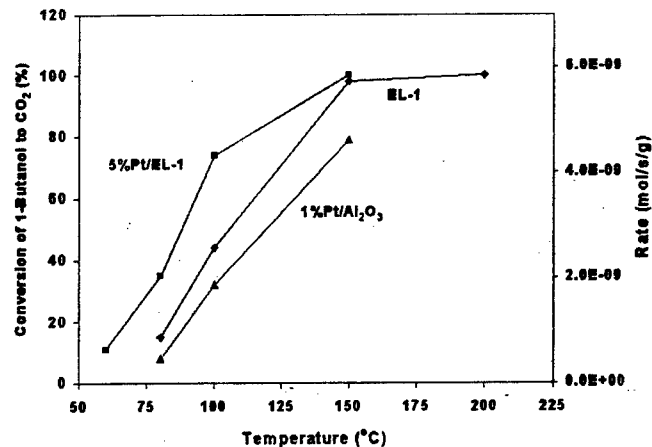
**Fig. 10.** Comparison of activities of 5 wt% Pt/EL-1, EL-1, and commercial 1 wt% Pt/Al$_2O_3$ for conversion of 1-butanol to CO_2. The 1-butanol concentration was approximately 100 ppmv in air and the space velocity was approximately 6,000 h^{-1}.

temperature was increased from 350 to 700°C there was a dramatic loss of low-temperature activity. At 80°C, the sample reduced at 350°C generated 66% conversion compared to only 18% for the sample reduced at 700°C. Since all three samples were heated at 200°C in air prior to screening, any reduced metals in the support material from the pretreatment likely were reoxidized, and the disparity in activity was not the result of chemical differences. It is more probable that higher temperature reduction resulted in greater sintering of Pt particles as demonstrated in the literature for similar catalysts (Bernal et al. 1999). Furthermore, reductive pretreatment was not necessary to generate Pt metal, and the improved activity likely was due to greater removal of nitrate precursor ions in a H_2 atmosphere. At reduction temperatures below 350°C, nitrate from the Pt precursor remained on the surface [as indicated by Fourier transform infrared (FTIR) spectroscopy] and deactivated the catalyst. Therefore for Pt analogs the goal was to achieve a reduction temperature that removed residual nitrate with minimal sintering of Pt particles. Under oxidative conditions, much higher temperatures were necessary to eliminate residual nitrate, which had a detrimental effect on the catalyst characteristics.

Fig. 10 contains a direct comparison of activity versus temperature for a commercial 1%Pt/Al$_2O_3$, EL-1 without Pt, and 5 wt%Pt/EL-1. The Pt/EL-1 catalyst was reduced at 350°C and, as expected, demonstrated a significant improvement in low-temperature activity for OV destruction. At 150°C, conversion of 1-butanol to CO_2 was equivalent for EL-1 and Pt/EL-1; however, at 100°C inclusion of Pt increased conversion from 44 to 74%, and at 80°C conversion increased from 15 to 35%, relative to the Pt-free analog. Furthermore, the Pt/EL-1 catalyst demonstrated 11% conversion at only 60°C.

Within the range of metal oxides used as carriers for these Pt analogs, activity was not highly dependent on the carrier composition. In fact, results for Pt/CeO$_2$ were roughly equivalent to those for Pt on modified CeO$_2$. Activity likely could be improved by increasing the extent of Pt dispersion on the carrier. For a given quantity of Pt, increasing dispersion corresponds to a decrease in Pt particle size, which would generate a greater number of active sites by increasing Pt surface area, and increasing the three-phase boundary area between the metal, metal oxide, and gas phase. Moreover, it also has been suggested that particle dimensions for very small clusters of atoms could be adjusted to
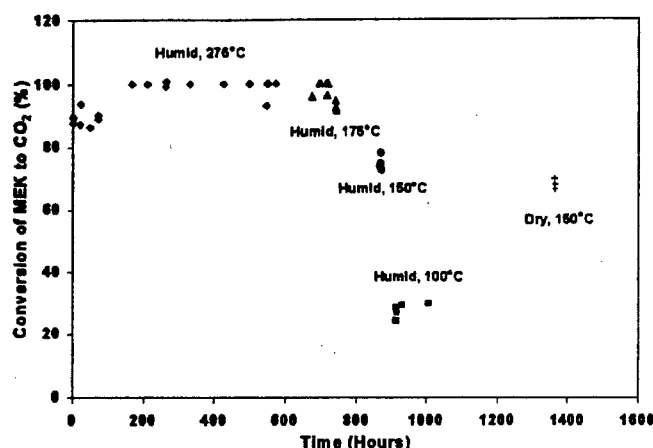
Fig. 11. Conversion of MEK to CO_2 over time in moist air for monolith-supported EL-5. The MEK concentration was approximately 100 ppmv in air and the water vapor content was approximately 45 mg/L. The $W/F \approx 0.5$ g s/cm^3.

Fig. 12. Conversion of n-butylamine to CO_2 during 386 h on stream. The catalyst was monolith-supported EL-5, and the n-butylamine concentration was approximately 1000 ppmv in air. The $W/F \approx 1$ g s/cm^3.

activate the oxidation process through beneficial electronic interactions between the particle and reactants (Heiz et al. 1999). For example, unexpected peaks in activity and particle size dependency for oxidation of CO were observed for Au clusters consisting of about 300 atoms (Valden et al. 1998) and Pt clusters of only 15 atoms (Heiz et al. 1999). Others also have demonstrated size dependence of noble metal particles for CO oxidation (Haruta et al. 1993; Haruta 1997), and similar processes might exist for OV oxidation as well. However, the mechanism for oxidation of OVs is different than for CO. The advantages gained by small Au and Pt clusters for CO oxidation are attributed to enhanced dissociation of O_2 (Haruta et al. 1993; Haruta 1997; Valden et al. 1998; Heiz et al. 1999), which does not appear to be the limiting process for OV oxidation (Batiot and Hodnett 1996; O'Malley and Hodnett 1997, 1999). Whether simply increasing the number of active sites or creating electronic interactions, the challenge for synthesizing these catalysts will be attaining high dispersions of active metals using practical preparation methods.

Catalyst Stability

Monolith-supported EL-5 catalyst was tested for long-term stability in the presence of water vapor, as well as nitrogen-, chlorine-, sulfur-, and phosphorus-containing organic compounds. Fig. 11 summarizes results for destruction of MEK over a 1000 h period in the presence of moisture. Moisture vapor was introduced by flowing the air line in Fig. 1 through a heated water bubbler. This configuration enabled a moisture vapor content of approximately 45 mg/L (roughly 90% relative humidity at 38°C) to be maintained over the duration of the experiment. As shown in Fig. 11, there was a gradual increase in MEK destruction over the first 200 h, then complete destruction was maintained at 275 and 175°C for over 740 h total. Conversion of MEK to CO_2 dropped below 80% at 150°C, then below 40% at 100°C, and this level of conversion was maintained for 94 h before terminating the test. The catalyst was heated in dry air at 250°C for over 100 h to remove moisture, then tested for destruction of MEK at 150°C under dry conditions. In the absence of moisture, about 70% conversion of MEK to CO_2 was achieved at 150°C, which was slightly lower than with moisture. Equivalent results were obtained for other catalyst compositions using toluene and 1-butanol as the test OVs, and generally, moist conditions improved OV destruction by a few percent.
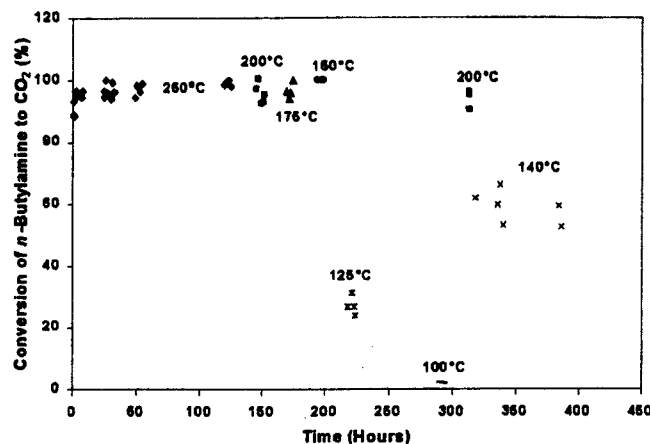
Monolith-supported EL-5 was very stable in the presence of a nitrogen-containing compound. The results are summarized in Fig. 12 for 386 h on stream with n-butylamine ($\approx$1000 ppmv in air) over a range of temperatures. During the first 200 h, complete conversion (of the butyl group) to CO_2 was maintained at temperatures between 150 and 250°C. Decreasing the temperature to 125°C reduced conversion to about 27% during a 24 h period, and at 100°C conversion was only about 2%. Nearly complete conversion was restored upon increasing the temperature back to 200°C. The remaining 69 h of testing were performed at 140°C, which maintained ~60% conversion.

Similar results were obtained for conversion of 1-chlorobutane ($\approx$490 ppmv in air) using monolith-supported EL-5, as shown in Fig. 13. At 250°C, approximately 60–70% conversion was maintained for the duration of the test. Lowering the temperature to 200°C decreased conversion to about 11%, and at 175°C conversion was only a few percent.

Fig. 14 presents results for stability of monolith-supported EL-5 against sulfur and phosphorus poisoning. For these tests, conversion of thiophene ($\approx$410 ppmv in air) and dimethyl meth-
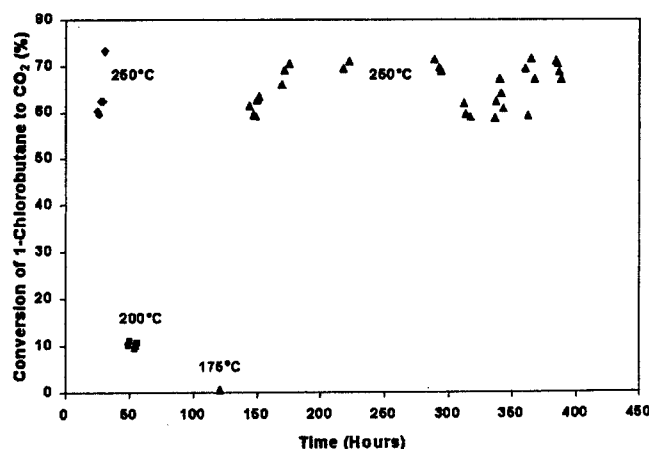
Fig. 13. Conversion of 1-chlorobutane to CO_2 during 388 h on stream. The catalyst was monolith-supported EL-5, and the 1-chlorobutane concentration was approximately 490 ppmv in air. The $W/F \approx 1$ g s/cm^3.
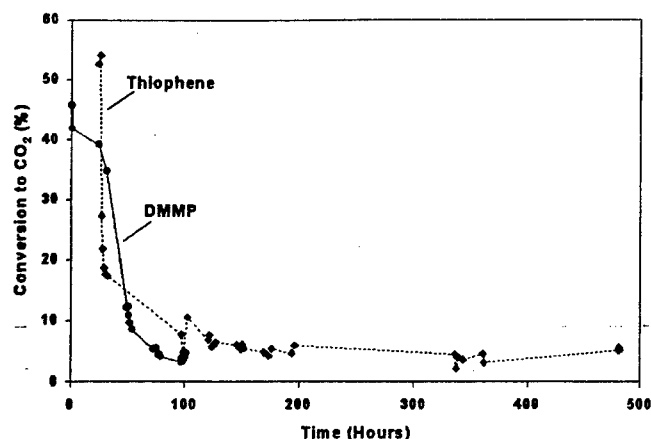
Fig. 14. Conversion of thiophene (dotted line, ≈ 410 ppmv in air) and DMMP (solid line, ≈ 1250 ppmv in air) to CO_2 over time. The catalyst was monolith-supported EL-5 and $W/F \approx 0.5$ g s/cm^3. The temperature was 250°C for the entire test.

ylphosphonate (DMMP, ≈ 1250 ppmv in air) to CO_2 was measured at 250°C. As evident in Fig. 14, results from these tests were much less encouraging than for moisture, nitrogen, and chlorine. Activity began to drop off immediately, and after only 100 h on stream, conversion was less than 10%. Conversion stabilized at about 5% for thiophene for the remaining 482 h on stream. As anticipated, FTIR analysis of the catalysts indicated formation of sulfates and phosphates after the thiophene and DMMP tests, respectively. The thermodynamics of sulfate and phosphate formation for the constituents of this catalyst are very favorable, and modifications to this composition are necessary to target compounds containing these species.

Summary and Conclusions

Modified CeO_2 catalysts tested in this work demonstrated high activity for low-temperature destruction of the common solvents toluene, 1-butanol, and MEK. Under practical conditions, these catalysts (without precious metals) generated complete conversion of 1-butanol to CO_2 at 150°C, 69% conversion at 100°C, and 15% conversion at 80°C. For toluene, complete conversion was achieved at 200°C, and greater than 75% conversion at 150°C. Similar results were obtained for MEK, and the most active materials outperformed commercial 1%Pt/Al$_2$O$_3$ in side-by-side comparisons. These results highlighted the beneficial synergy that can be achieved by compositing CeO_2 with transition metal oxides.

Standard commercial cordierite monoliths worked very well as catalyst supports, and catalyst-coated monoliths were structurally rugged, reproducible, and as active as the powder analogs. The deposition method made it easy to achieve the target composition, which facilitated catalyst optimization. Monolith-supported catalysts were stable in moisture and resisted poisoning from nitrogen- and chlorine-containing organic compounds. However, the catalysts quickly deactivated in the presence of sulfur and phosphorus compounds due to the formation of sulfates and phosphates.

Incorporation of Pt generally improved OV conversion rates, but activity was not highly dependent on the composition of the carrier within this limited range of CeO_2-based compositions. It is

likely that the practical laboratory method used for deposition of Pt was not capable of achieving metal particle characteristics necessary for enhanced activity.

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